7/6/78

EEB BRANCH REVIEW

DATE: IN _____ OUT _____ IN 5/24/77 OUT 7/6/78 IN _____ OUT _____

FISH & WILDLIFE ENVIRONMENTAL CHEMISTRY EFFICACY

FILE OR REG. NO. 464-LUA

PETITION OR EXP. PERMIT NO. _____

DATE DIV. RECEIVED 5/10/77

DATE OF SUBMISSION _____

DATE SUBMISSION ACCEPTED 3C1D-2A-4C5

TYPE PRODUCT(S): I, D, H, F, N, R, S Herbicide

PRODUCT MGR. NO. #25

PRODUCT NAME(S) Garlon 3A Herbicide

COMPANY NAME Dow Chemical

SUBMISSION PURPOSE Reg: New Chemical: Non-crop areas: including forests.

CHEMICAL & FORMULATION Triclopyr= 3,5,6-trichloro-2-pyridinyloxyacetic acid, as as triethylamine salt. Contains 3 pounds per gallon.

1. Introduction.

Applicant proposes registration of the new active herbicide ingredient 3,5,6-trichloro-2-pyridinyloxyacetic acid, as the triethylamine salt. The active ingredient has an common name of Triclopyr for the acid, so that it could also be referred to as triclopyr triethylamine salt. The formulated product is called Garlon 3A Herbicide and contains 44.4% active ingredient as the salt, which is equivalent to 31.8% acid equivalent and is present in the formulated product at 3 pounds acid equivalent per gallon. The label for the formulated product also states just below the ingredient statement "Contains methanol". The product is intended for use for the control or suppression of woody plants and broadleaf weeds on rights-of-way, forests, and industrial sites.

Previous reviews of this active ingredient may be found in EUP's under the code names of M-3724 Herbicide, Dowco 233, and Grazon 3.

2. Directions for Use

Use ½ to 1 gallon of Garlon 3A to make 100 gallons of spray and use 100 to 400 gallons of spray per acre. (1.5 to 12 pounds active ingredient per acre). Tank mix with DMA 4, Esteron 99 or Tordon 101 using ¼ to ½ gallon of Garlon 3A per 100 gallons of spray. For forest site preparation use 3 to 6 pounds active ingredient per acre or tank mix with Esteron 99 or Tordon 101. Note: Do not plant conifer seedlings on treated areas for at least 6 months after applying Tordon 101 in such a tank mix.
Do not apply Garlon to vegetable crops or ornamentals.
Do not contaminate irrigation ditches or water used for irrigation or domestic purposes. Do not graze treated areas or feed treated forage.

Garlon 3A Herbicide is recommended for the control of unwanted woody plants and annual and perennial broadleaf weeds on non-crop areas including forests, industrial manufacturing and storage sites, rights-of-way such as electrical power lines, communication lines, pipelines, roadsides and railroads.

Reference 2
Aerobic Degradation of Ring-Labeled 14C-3,5,6-Trichloro-2-pyridyloxyacetic Acid in Soil.
A. J. Regoli, D. A. Laskowski
Report No. GS-1364. April 17, 1974

Triclopyr was radiolabeled in the 2- and 6- positions. Two soils were tested: Yolo (Davis) with 50% sand, 34% silt, 16% clay, pH 6.5, organic carbon 0.8%, 1/3 bar moisture 21.8%, and classified as a loam; Flanagan (Geneseo) silty clay loam with 14% sand, 54% silt, 32% clay, pH 5.8, organic carbon 4.2%, and 1/3 bar moisture 26.3. The treatment rate in both soils was 1 ppm. Both soils were incubated at temperatures of 15 and 35°C, and at 32% and 100% of 1/3 bar moisture for intervals of up to 375 days. Evolved $^{14}CO_2$ was measured, as well as acidified ether extractable 14C, sodium hydroxide extractable 14C, and non-extractable 14C remaining in soil after the extraction procedures. Standard radioassay procedures were used to determine 14C. The acidified ether extractable 14C was examined by tlc to determine the nature of the 14C-moiety.

Results:

Material balance was good for all treatments, with an average of 97%, a range between 87.7% and 104.3%, and standard deviation of 3.96%.

The major portion of 14C was found in the acidified ether extract of the soil, followed by evolved $^{14}CO_2$. Non-extractable 14C amounted to 12.5% in silty clay loam (32% moisture held at 35°C) at 255 days, but the average non-extractable 14C over all treatments was 3.8% of the applied radioactivity.

The evolution of $^{14}CO_2$ was significant in both soils, with certain amount of dependency upon moisture and temperature. The evolution of $^{14}CO_2$ ranged from lows in both soils at 15°C and the lower moisture of 7.1% and 8.9% at 373 days to highs of 25-30% at higher temperature and higher moisture at 250 days. The

$^{14}CO_2$ evolution indicates that portions of the ring structure is being broken.

The degradation of triclopyr is temperature dependent, with the higher temperatures causing more degradation of triclopyr than the lower temperatures. The higher temperature resulted in degradation to 10% or less of the initial amount by day 250. The higher temperature also showed greater amounts of the degradate 3,5,6-trichloro-2-pyridinol and showed decline of this degradate at the longer sample intervals. The degradate 3,5,6-trichloro-2-pyridinol accounted for up to 60% of the appleid radioactivity in some samples. Another degradate 3,5,6-trichloro-2-methoxypyridine was also found in the later intervals but not at levels as high as the trichloropyridinol

There was very little unidentified radioactivity in the soils.

Conclusions:

Triclopyr degrades in soil, with evolution of $^{14}CO_2$, formation of trichloropyridinol and trichloromethoxypyridine. The rate of degradation of triclopyr at 35°C calculates into a halflife of between 10 and 46 days, but 35°C is not an environmentally expected temperature. At the more probable environmental temperature of 15°C, the calculated halflife range is between 79 and 361 days, dependent upon soil type and moisture content, and probably upon the organic carbon content of the soil. The expected halflife of triclopyr in the degradation process from parent compound through trichloropyridinol and trichloromethoxypyridine to CO_2 is much greater than the above calculated halflife for the parent compound only.

Reference 3
Aerobic Decomposition Rates of 14C-Triclopyr in Several Soils. (Status Report).
D. A. Laskowski, H. D. Bidlack, L.B. Comeaux
Report No. GH-C-863. Oct. 16, 1975.

Four soils were treated with 14C-triclopyr labeled in the 2 and 6 position of ring. Concentration in the soil was 1 ppm. Treated soils incubated at three temperatures in soil biometer flasks. Triclopyr extracted from soil by shaking 5 grams soil with 10 ml of 0.1 M HCl or 1.5 M H_3PO_4 and 15 ml of diethylether. Soil aliquots combusted and counted; other aliquots to TLC and then counted.

Results:

Results are reported as % of parent compound remaining in soil. There is no material balance of 14C nor identification of other 14C-containing compounds.

Halflife of parent compound at 25°C and 35°C was less than 50 days in 3 soils. Three halflives of parent ranged up to 249 days. The fate of non-parent compound is unknown.

At 15°C, a more probable environmental temperature, the first halflife in two soils ranged from 79 to 156 days while three halflives ranged up to 370 days.

Conclusions:

The study is indicative of the laboratory rate of the first degradation of parent triclopyr but does not describe mode or mechanism. The rate of degradation as shown in the laboratory is probably faster than could be expected in the natural environment. The temperature dependency may be indicative that microorganisms may be resposible for the degradation.

Reference 4
Degradation of 14C-Troclopyr in Sterile and Non-Sterile Soil.
P. J. McCall, D. A. Laskowski, T. K. Jeffries
Report No. GH-C-960. Dec. 28, 1076.

Commerce silt loam soil was treated with radiolabeled triclopyr with 14C in the 2 and 6 position at rate of 9 ppm. Soil was sterilized by steam treatment of one hour each day for three days. Soil samples were incubated at 25°C. Evolved 14CO2 was trapped. Soil aliquots from each treatment were combusted and counted, or extracted with acidified ether, followed by sodium hydroxide extraction, and extracted soils were then combusted for total 14C. The chemical nature of the 14C was examined by TLC

Results:

Material balance for the sterile samples was good, at 97% of applied. Non-sterile soil samples showed high recovery which was later discovered to be due to miscalculation of the amount of staring soil. Most of the initial amount of 14C was extracted in the acidified ether, with little appearing in other portions of the procedure.

The sterile soil samples showed essentially no evolution of 14CO2 during 56 days of incubation. The extract of the sterile soil showed only parent compound with no indication of any other degradates.

The non-sterile soil samples were incubated for 101 days and showed evolution of 14CO2 of 19%, along with the formation of 3,5,6-trichloro-2-pyridinol of up to 32% of initally applied radioactivity and small traces of secondary degradate 3,5,6-trichloromethoxypyridine at 2.6%. Applicant calculates the halflife of parent triclopyr to be about 69 days in non-sterile soil incubated at 25°C for up to 101 days. The temperature is higher than would be expected in the environment.

Conclusions:

Triclopyr does not degrade in Commerce silt loam soil which has been sterilized, but does degrade in the same soil which is not sterile. Micro-organisms therefore appear to play a role in the degradation of triclopyr.

Non-sterile soil showed degradation of triclopyr to 3,5,6-trichloro-2-pyridinol and then to 3,5,6-trichloromethoxypyridine and eventually to carbon dioxide.

Reference 5
Comparison of the Degradation Rates and Decomposition Products of 14C-Triclopyr in Aerobic and Waterlogged Soil.
H. D. Bidlack, D. A. Laskowski, R. L. Swann, L. B. Comeaux, T. K. Jeffries
Report No. GH-C-919. June 22, 1976.

Two soils were used to determine the degradation of triclopyr under aerobic and anaerobic conditions. The two soils were an Illinois silty clay loam and Mississippi silt loam. Another soil, Yolo loam was used in amendment study. The soils were maintained under aerobic conditions, or under aerobic conditions for 30 days followed by waterlogging, or by waterlagging at day zero. Evolved $^{14}CO_2$ was trapped. Aliquots of the incubated soils were counted, other aliquots were extracted with acidified ether then by sodium hydroxide and residual 14C counted. Extracts examined by TLC. Supernatant water was extracted with acidified ether and examined by TLC. In the amendment study, the loam was amended by the addition of 1% ground alfalfa or fertilizer, or held at higher incubation temperature.

Results:

Aerobic soils incubated at 25°C showed evolution of $^{14}CO_2$ of between 70-79% of applied 14C during 300 days of incubation, while parent triclopyr remaining accounted forless than 5% at 300 days. When the same soils were waterlogged after 30 days of aerobic exposure, the evolution of $^{14}CO_2$ after 300 days was the same in the silt loam and somewhat reduced in the silty clay loam but still evolving. The amount of parent triclopyr remaining as parent after 300 days in the aerobic waterlogged experiment was less than 5%. In the two soils maintained under waterlogged conditions for the entire 300 days, the evolution of $^{14}CO_2$ was considerably reduced and delayed. In the waterlogged silt loam the $^{14}CO_2$ evolution did not occur to a significant degree under after about 100 days of incubation, while in the waterlogged silty clay loam the delay was until about 200 days.

Reference 5 (continued, pag -)

In both the waterlogged soils, the parent triclopyr partitioned into the water phase to the extent of 60-75%, followed by a slight return to the soil phase and degradation. The degradate 3,5,6-trichloro-2-pyridinol is found in both the water and soil phases and it cannot be determined whether the degradate is formed in the soil and transferred to the water, or whether the degradate is formed also in the water. There is generallly greater amounts of the degradate trichloromethoxy pyridine in the water phase than in the soil phase. The trichloromethoxypyridine is not found until after the formation of trichloropyridinol.

The halflife of parent compound under aerobic conditions is calculated by the applicant to be 18 days in silt loam and 8 days in silty clay loam, while under waterlagged conditions the halflifes are 130 and 42 days respectively. These halflifes ignore the presence of the two degradates trichloropyridinol and trichloromethoxypyridine which may have adverse effect on the environment. The calculated halflifes are shorter than found in other studies in which the soil was incubated at higher or lower temperatures, which indicates that the 25°C incubation temperature used in this study is probably more optimum for microorganism growth and degradation of triclopyr by microorganisms than the other incubation temperatures.

In the amendment portion of the experiment, the Yolo loam without added alfalfa showed slower degradation of triclopyr than other soils, but with the added alfalfa the degradation was faster but still not equal to the other two soils tested. Incubation of the Yolo loam at 35°C slowed the degradation rate. The addition of fertilizer to the Yolo loam gave carbon dioxide evolution intermediate between added alfalfa and the higher temperature, but had essentially no effect on the silt loam or the silty clay loam,

Conclusions:

Under aerobic conditions the rate of degradation of triclopyr to trichloropyridinol and eventually to carbon dioxide is faster at 25°C than at 35°C which in turn is faster than at 15°C. This indicates microbial degradation processes are involved.

The degradation of triclopyr is much slower under waterlogged conditions than under aerobic conditions, with aerobic degradation 5-8 times as fast as the degradation under waterlogged conditions. The products of degradation under aerobic or waterlogged conditions are the same: trichloropyridinol, trichloromethoxypyridine, and eventually carbon dioxide. Under waterlogged conditions, triclopyr, trichloropyridinol, and trichloromethoxypyridine are present in the water phase to a significant degree, indicating water solubility. Additional organic matter added to soil increases the rate of degradation of triclopyr, while the addition of fertilizer does not have this effect.

Reference 6
Metabolism of 3,5,6-Trichloro-2-pyridinyloxyacetic acid (Triclopyr) in Grass and Soil
R. W. Meikle
Report No. GS-1442. June, 1976.

Triclopyr radiolabeled in the 2 and 6 positions was applied to small plots of established lawn at a rate equivalent to 3 pounds per acre. Samples of grass clippings and soil were obtained at intervals up to 370 days after application for clippings and at 428 days for soil. Grass clippings were analysed by standard radiometric assay procedures before and after extraction, and acid hydrolysis. TLC was used to identify degradates. Soil samples extracted with acidified ether and then by sodium hydroxide. Triclopyr in formulation.

Results:

Seven days after application, triclopyr parent compound was the major portion of the recoverable radioactivity. At all other sample intervals later than 7 days, triclopyr was not the major residue. By day 42 and thereafter, the major portion of the radioactivity was present in water-soluble polar unknowns and non-extractable material, and comprised 88% of the recovered ^{14}C. At day 42 parent compound was 0.03 ppm in the grass, along with a conjugate of parent at 0.19 ppm. By days 123 and 370, the amount of recovered parent triclopyr was less than 0.1 ppm for combined parent and conjugated parent.

The degradate trichloromethoxypyridine constituted 23 ppm residue at the 7 day interval but declined to 0.06 ppm by day 74. Applicant postulated that trichloromethoxypyridine is formed via photochemical processes on the surface of the grass leaves. The amount of trichloropyridinol found at any sample interval was 0.25ppm or less.

Soil samples taken at 428 days showed about 0.4 ppm of ^{14}C expressed as triclopyr. Triclopyr per se was 0.001 ppm and trichloropyridinol was 0.002 ppm in the soil at this time with the remainder in humic and fulvic acids (69%)

and some (27%) in humin.

Several unknown conjugates were found, at levels of less than 1% of the total recovered radioactivity, but acid hydrolysis did not release any recognizable fragments.

Conclusions:

Residues of triclopyr decreased from 187 ppm equivalent to less than 1 ppm equivalent in grass in 128 days. Soil residues of triclopyr at 428 days after application were extremely low.

Triclopyr is degraded in the environment and its degradation products are in turn again degraded, eventually becoming unextractable fractions in grass and in the humic and fulvic acid, and in humin in soil.

Reference 7
Aerobic Degradation of 3,5,6-Trichloro-2-pyridinol in 15 Agricultural Soils.
H. D. Bidlack.
Report No. GH-C-991. April 19, 1977.

The test compound 3,5,6-trichloro-2-pyridinol is a degradate of the herbicide triclopyr, and also a degradate of the insecticides chlorpyrifos and chlorpyrifos-methyl. The compound was radiolabeled in the 2 and 6 positions. Trichloropyridinol was added to 15 soils from 10 major agricultural ares at the rate of one ppm. The treated soils were incubated in biometer flasks for appropriate intervals up to 300 days at 25°C. The flasks were maintained in aerobic condition. Evolved $^{14}CO_2$ was trapped. Soil aliquots were counted by standard radiometric assay procedures, while other aliquots were extracted with acidified diethyl ether followed by sodium hydroxide extraction. Extracts were counted for radioactivity and subjected to TLC analysis to determine the identity of the ^{14}C material. Soil characteristics are given.

Results:

Evolved $^{14}CO_2$ was the major reservoir of ^{14}C material in most soils at 300 days, accounting for between 14.3% to 81.6% of the applied ^{14}C, with a mean of 57.6% of applied ^{14}C evolved as $^{14}CO_2$ in the 15 soils.

Non-extractable ^{14}C remaining in soil was less than 10% in all soil samples and generally less than 5%. At 56 days of incubation, the mean % of nonextractable ^{14}C was 5.4% and did not change much thereafter.

The degradate trichloromethoxypyridine was found at levels up to 24% in several soils, but generally occurred at much lower levels. However, the data do not indicate degradation of trichloromethoxypyridine occurs to a great extent, although several soils do show decline.

Two other unidentified 14C moieties were found in the acidified ether extract of the soil, one occurring up to 6.5% and the other up to 1.8% maximum.

The maximum amount of 14C which was extracted into cold sodium hydroxide was 16.5%. The overall mean for all samples in all soils is 8.3 ppm. When this radioactivity is separated into high molecular weight components, most of the 14C occurs in materials with molecular weight over 2000, indicating that the 14C is in the organic matter of the soil.

The halflife of trichloropyridinol in the various soils ranged from 8 days to 279 days, with no apparent correlation with storage time, organic carbon content or soil texture or class. Eight soils showed halflife of less than 50 days, while twelve soils showed halflife of 90 days or less.

Conclusions:

The degradate of triclopyr, trichloropyridinol, is in turn degraded with evolution of carbon dioxide, the formation of some trichloromethoxypyridine, and incorporation into the soil organic matter. The rate of such degradation of trichloropyridinol is highly variable, with no apparent correlation to soil characteristcs, organic carbon content of texture. The data support the applicants hypothesis that triclopyr degradates are in turn redegraded.

Reference 8
Aerobic Soil Decomposition of 14C-Labeled 3,5,6-Trichloro-2-methoxypyridine.
D. A. Laskowski, L. B. Comeaux, H. D. Bidlack
Report No. GH-C-964. February 11, 1977.

The test material, 3,5,6-trichloro-2-methoxypyridine has been shown to be a degradate of the herbicide triclopyr. Therefore it is of interest to determine if the degradate is in turn redegraded. The trichloromethoxypyridine was radiolabeled in the ring. Three soils were studied in this experiment, using two lots of esch soil collected at different times of the year. The different lots of soil were stored in the laboratory under different conditions, one lot was air-dried and stored at -34°C, while the other was stored at field moisture content at 4°C. Soil characteristics are given for the Commerce silt loam, the Flanagan silty clay loam, and the Yolo loam. The soils were treated with trichloromethoxypyridine at the rate of 1 ppm, placed in soil biometer flasks and incubated for intervals up to 300 days at 25°C in the dark. Evolved carbon dioxide was trapped. Soil moisture levels were either 100% of 1/3 bar or 35% of 1/3 bar moisture content for incubation.

Results:

There is no apparent difference in the rate of degradation of trichloromethoxypyridine based upon soil lots collected in winter versus those collected in the summer. There is no apparent difference in the rate of degradation of trichloromethoxypyridine based upon differences in the manner of storage of soil after collection, whether at -34°C or at 4°C.

The soil moisture content did show some differences in the rate of degradation of trichloromethoxypyridine, with faster degradation at higher moisture contents. In another study, the degradation of triclopyr showed

higher accumulation (slower degradation) of trichloromethoxypyridine at higher moisture levels than at lower moisture levels. This finding was not confirmed in the current study, which showed faster degradation of trichloromethoxypyridine at the higher than at the lower moisture contents.

The evolution of $^{14}CO_2$ was quite extensive from both the Commerce silt loam and the Flanagan silty clay loam, with 60% or more of the initially applied 14C evolved from both soils when held at 100% of 1/3 bar for intervals of 300 days. The Yolo loam, which the applicant states is a "known poor degrader soil", showed only 11.4% evolution of the initial 14C as $^{14}CO_2$.

The only other degradate found in this study was trichloropyridinol, which is also a degradate of triclopyr. The trichloropyridinol accumulated in the Flanagan silty clay loam to a maximum of 29% of the applied radioactivity. The other two soils showed lesser amount of trichloropyridinol, and in the longer duration intervals, the trichloropyridinol showed some decrease in the amount of 14C present in that form. Other studies using trichloropyridinol as the starting test material showed that trichloromethoxypyridine as a degradate trichloropyridinol, while this current study shows that trichloropyridinol is a degradate of the trichloromethoxypyridine. Applicant states that the reaction between the two compounds is reversible and is probably driven by microbial activity.

There was very little unidentified 14C in the extracts of the soil, and very little 14C was not extractable from the soils.

Coclusions:

Trichloromethoxypyridine degrades to carbon dioxide and trichloropyridinol in two soils, with estimated halflives of about 50 days, but another soil , Yolo loam shows 30% conversion to carbon dioxide and trichloropyridinol in 300 days.

Reference 8 (continued, page 5)

Another study show the degradation of trichloropyrindinol to trichloromethoxy-pyridine while this study shows the degradation of trichloromethoxypyridine to trichloropyridinol, indicating that the degradation is reversible. The evolution of carbon dioxide however indicates that further degradation occurs to a large degree in several soils.

Reference 9
Laboratory Study on the Degradation of Triclopyr Alone and in Combination With (2,4-Dichlorophenoxy)Acetic Acid and Picloram in Soil as a Simulated Tank Mix.
R. L. McKellar, R. D. Glas, B. L. Johnson, D. A. Laskowski.
Report No. GH-C-990. April 14, 1977.

Two soil types were used in this tank mix degradation study. Both soils are known degrader soils for triclopyr, from other soil degradation studies. The two soils are Commerce silt loam and Flanagan silty clay loam, with soil characteristics described. Each soil was treated with triclopyr alone,at 6 ppm; triclopyr 6ppm plus 8 ppm of 2,4-D; 6 ppm triclopyr plus 4 ppm 2,4-D plus 1 ppm picloram; 4 ppm 2,4-D; 8 ppm 2,4-D; and 1 ppm picloram. Treated soil samples were incubated at 25°C for intervals of up to 300 days. After incubation, the soils were analysed for parent compounds remaining in soil undegraded. Analytical methods are given for picloram and 2,4-D but not discussed herein. Triclopyr is extracted from soil by heating in methanolic alkaline solution. After alkaline hydrolysis, a portion is acidified and triclopyr partitioned into benzene and cleaned up on alumina column which retains the triclopyr. The triclopyr is eluted from the column by dilute sodium hydroxide, acidifed, and returned to benzene solution. Triclopyr is converted to its methyl ester by reaction with boron trifluoride-methanol reagent. The methyl ester is quantified by glc using electron capture detector. Recovery by this method is reported to be 78±3% between 0.01 to 5.0 ppm.

The triclopyr degradate 3,5,6-trichloro-2-pyridinol is extracted somewhat similarly, but eventually reacted with N,O-bis(trimethylsilyl)acetamide to form trimethylsilyl pyridinol derivative for glc using electron capture detection.

The triclopyr degradate 2-methoxy-3,5,6-trichloropyridine is also extracted

in a similar manner, but it is not necessary to form a derivative, in that 2-methoxy-3,5,6-trichloropyridine will chromatograph directly. Recovery for these two degradates are reported to be 96±3 and 90±3%

Results:

Residues of parent triclopyr alone or in combination with 2,4-D and/or picloram declined from an average of 6.6 ppm at day zero to 0.09 ppm at 200 days, while the triclopyr degradate trichloropyridinol increased to 2.5 ppm at 56 days and declined thereafter to 0.79 ppm at day 200 and the other degradate methoxytrichloropyridine increased to 0.48 ppm at 100 days and declined to 0.24 ppm at 200 days. The halflife of triclopyr was found to be an average of 29 days over the various treatments, with a range of 16 to 48 days. These halflifes are at the shorter end of expected persistence of triclopyr, since other soils have shown halflifes several times as long. The data indicate that triclopyr degrades into trichloropyridinol and then into trichloropyridine, and these two compounds comprised approximately 15% of the initial amount of triclopyr.

There was no apparent effect on the rate of degradation of triclopyr from the presence of 2,4-D and/or picloram as mixtures. There was no appraent effect on the rate of degradation of either 2,4-D or picloram due to the presence of triclopyr.

Conclusions:

There is no apparent effect on rates of degradation of triclopyr, 2,4-D, or picloram when applied to soils alone or in combination with each other.

Reference 10
Residues of Triclopyr, 3,5,6-Trichloro-2-pyridinol, and 2-Methoxy-3,5,6-trichloropyridine in Soil Treated with Garlon 3A Herbicide.
R. L. McKellar
Report No. GH-C-983. April 11, 1977.

Field test plots located in six states were sprayed by ground application of Garlon 3A at the rate of three gallons per acre, (9 pounds active ingredient per acre) and soil samples were collected from the test plots at intervals of up to 477 days after application. The residues of parent triclopyr, and its degradates trichloropyridinol and methoxytrichloropyridine were analysed by the analytical procedures described in reference 9 above. The six locations and soils are:

Tifton, Georgia, loamy sand
Fargo, North Dakota, clay
Corvallis, Oregon, hazelaire comples
Benchley, Texas, clay to clay loam
Arthurdale, West Virginia, unspecified soil
Laramie, Wyoming, Forelli fine sandy loam

Results:

Residues of parent triclopyr had an average halflife of 46 days, with a range of halflifes between 18 and 84 days. The residues of parent triclopyr were quite variable in the different soils at the start of the tests. For example, the Georgia loamy sand showed 6.9 ppm of triclopyr the day of application, while the North Dakota soil showed 0.01 ppm at day zero and only 0.21 ppm at day 28. These are extreme examples and the other soils showed between 0.5 ppm and 3.0 ppm at the start of the experiment. The density of ground cover could explain some of the difference but probably cannot account for the entire amount of difference. In any case, the amount of parent triclopyr declined throughtout the study to 0.22 ppm or less in five soils at 400+ days.

The degradate trichloropyridinol showed maximum residues in the 0-6 inch soil layer between 28 and 56 days after application and declined thereafter.

The degradate trichloro-methoxy-pyridine did not show a maximum residue at any specific interval, but remained generally around 0.1 ppm or less at all sample intervals.

There is little or no evidence of leaching of the parent compound or its degradates, since the 6-12 and 12-18 inch soil layers showed only low levels of the three compounds, unless of course, the leaching was so rapid that the 28 day sample interval was too long and the residues had already leached below the 18 inch soil layer. While this is possible, other data indicate the the rate of leaching of triclopyr and its degradates is not that great.

Conclusions:

Triclopyr and its degradates decline to levels of 10% of the initial amount or less in approximately 400+ days, with the degradate trichloropyridinol accumulating to some degree in the soil, and then declining to low levels. Trichloromethoxypyridine does not show evidience of accumulating to any degree. While triclopyr has a certain degree of persistence, its use pattern as a herbicide used once a year would preclude the buildup of triclopyr or its degradates in soil to any significant amount. The data indicate that triclopyr should be considered to be of moderate chroncity when its degradation is considered for possible adverse effects in wildlife.

Reference 11
Adsorption of Triclopyr in Soil
J. W. Hamaker
Report No. GS-1390, Feb. 6, 1975

Adsorption of 14C-triclopyr (2,6-14C) as the triethylamine salt to twelve soils investigated by the soil slurry method. The organic carbon content of the soils ranged from 0.081% to 21.7%. Adsorption coefficients (K_d) and (K_{oc}) were calculated.

Results

Adsorption coefficients (K_d) ranged from 0.016 to 14.5 while K_{oc} ranged from 12 to 78. In the soil desorption study of one soil, equilibrium was reached within 48 hours with about 1% remaining adsorbed

Conclusions:

When these results are classified as to mobility class and K_{oc} vlaues, triclopyr is classified as a mobile pesticide.

Reference 12
Adsorption of 3,5,6-Trichloro-2-pyridinol by Soils.
J. W. Hamaker.
Report No. GS-1354, 1974.

Adsorption of 3,5,6-trichloro-2-pyridinol radiolabeled in the 2,6 position was investigated by the soil slurry method in three soils, with organic carbon contents ranging from 0.5 to 3.6%. All three soils were classified as loam. Adsorption coefficients (K_d) and (K_{oc}) were calculated.

Results:

Adsorption coefficient K_d ranged from 0.634 to 5.64, while K_{oc} ranged from 114.0 to 156.5.

Conslusions:

The triclopyr degradate, 3,5,6-trichloro-2-pyridinol, is moderately adsorbed to loam soils, and would be classified as low (to intermediate) mobility. Trichloropyridinol is apparently less mobile than the parent compound.

Reference 13
A 45-Day Soil Leaching Test on Triclopyr ((3,5,6-trichloro-2-pyridinol)oxy) acetic acid.
J. W. Hamaker
Report No. GS-1469, February 7,1977.

Loam soil (sand 42, silt 49, clay 9, pH 6.2, organic carbon 0.62%) was used in the aged soil column leaching study. Duplicate soil samples were treated with the triethylamine salt of triclopyr at the rate of about 12 ppm. One sample was frozen and one sample was incubated aerobically for 45 days. Both soil samples were placed in soil columns and leached with 0.5 inch of water per day for 45 days. Leached soil and leachate were extracted by various procedures and standard radiometric assay techniques were employed.

Results:

The incubated soil had lost about 37% of the applied radioactivity during the 45 day incubation prior to addition onto the soil column. Of the 14C applied to the soil column after incubation, 75% leached through the twelve inch soil column, with very little 14C appearing before day 11 of leaching, peaking about day 15 and tapering off thereafter. The non-incubated soil showed essentially the same pattern of leaching, with about 82% of the applied 14C being eluted from the soil and with the same elution peak intervals. The incubated soil showed a second peak of elution of 14C from the soil column around day 24, indicating that another compound may be eluting. By tlc analysis, this second peak appears to be trichloropyridinol, a soil degradate of triclopyr.

The leached soil which had been incubated retained the major portion of the 14C in the first inch of soil in the column, while the non-incubated soil retained the major portion in the 5-inch segment of the column. Applicant

ascribes the differing retention of 14C to the degradation of triclopyr in the incubated soil, yielding trichloropyridinol, which is less mobile than is triclopyr. Trichloropyrindinol moved through the twelve inch column after about 13 inches of applied water, while triclopyr moved through the column after about 7.5 inches of water. No other degradates of triclopyr were XXXXXX identified, although there were small amounts of of 14C in other compartments of the system.

Conclusions:

Triclopyr is a leachable compound. Its soil degradate trichloropyridinol also leaches but to a lesser degree than the parent compound.

Reference 14
Column Leaching Studies with Triclopyr and Picloram - A Report -
Report by R. L. Zimdahl, Colorado State University.
Submitted to Dow Chemical Company, April 14, 1975.

A sandy loam soil (sand 64, silt 20, clay 14, pH 7.5, and 1.6% organic matter) was treated with 14C-triclopyr at unspecified rate. The position of the 14C in the triclopyr molecule is also unspecified. Soil columns were 4 inches or 12 inches long, with the top 1 inch layer being treated soil. Some treated soil aged 30 days prior to placement in soil column. Other soil leached after aging in the soil column. One column was leached continuously, while another was leached 5 days then allowed to dry 2 days, serially up to 28 days. Similat columns treated with picloram were leached in parallel manner. Each column was treated with 100,000 dpm. The analytical method is based upon 14C only; parent compound was not accounted specifically.

Results:

Average material balance in the five columns was 50.2% of applied 14C. Of the applied 14C, 37.3% was eluted through columns and 12.9% was retained in soil. However, of the accountable 14C, 74% leached through and 26% was retained in soil. Applicant provides no explanation of the low accountability. In parallel soil column using picloram, material balance was 97.9% with 85.9% eluted and 11% retained in soil.

There appears to be little difference between elution patterns of the 4 inch columns compared to the 12 inch columns. Study provides no information on the identity of leached or non-leached 14C or whether 14C is bound to soil since the soil samples were combusted without any extraction procedure.

No.	Column Length	Pretreatment	Eluate	Soil	Total
1	4	None	34.7%	4.5%	39.3%
2	12	None	31.1%	28.6%	57.9%
3	12	Aged 30 days	40.9%	13.3%	54.2%
4	4	Continuous Leach	40.3%	13.6%	54.0%
5	4	Intermittent	39.6%	12.9%	46.0%
		Average	37.3%	12.9%	50.3%

Conclusions: Laboratory Leaching Study:

Triclopyr is a leacher, but the chemical nature of the leached 14C is not known.

Field Leaching Study:

Triclopyr at rates of 0.5, 3.0, and 9.0 pounds active ingredient per acre was used to treat field soil contained in 6-inch steel cans which had been driven into the ground in the field. Experimental design precluded study of leaching and rate or mode of degradation. Measurement of persistence of phytotoxicity was performed by bioassay. Field soil was treated on unspecified date and sampled at monthly intervals. Soil from the sunken cans was sampled and planted to cucumbers. Evidence of persistence of phytotoxicity is shown by the dry weight yield of cucumbers as a percent of check cucumbers.

Results:

Triclopyr at rate of 0.5 lbs ai/A showed some inhibition of cucumber yield over period of at least 3 months, while triclopyr at rates of 3.0 and 9.0 lbs ai/A showed 50% inhibition of cucumber yield after a period of at least 4 months.

Conclusions:

Phytotoxic response of cucumbers is persistent. No analysis of soil residues of triclopyr to correlate with phytoresponse.

Reference 15
Behavior of Triclopyr (Dowco 233) in Soil and Stream Water on a Small Watershed, Southwest Oregon.
L. A. Norris, M. L. Montgomery, G. D. Savelle
Presented at Weed Science Society meeting, 1976 Annual Meeting, Denver, Col.

Triclopyr as the triethylamine salt was applied to a small watershed of approximately 4.25 acres at the rate of 3.0 pounds per acre by helicopter. The watershed is not specifically described other than as a "hill-pasture". The application was made in May, 1974. The watershed had a small intermittent stream, which does not flow during the dry summer months. The stream was dammed and equipped with flow meters, rain gauges, etc. The analytical procedure is only generally described and appears to be similar to the procedure used by Dow: alkaline methanol extraction, acidification, partition into benzene, and glc quantification. However, the authors do not state that the compounds were derivatized prior to glc. Triclopyr, trichloropyridinol, and methoxy-trichloropyridine were reported.

Results:

Overstory vegetation (not discussed or described) intercepted a large portion of triclopyr on the day of application. The following sample intervals showed that triclopyr eventually reached the soil from the overstory of vegetation. At the zero time sample interval, soil samples in the 0-5 cm zone contained 20 ppb of triclopyr, 7 ppb of trichloropyridinol, and 6 ppb of methoxytrichloro-pyridine. At the next sample interval at six months after application, the same soil zone showed 930 ppb of triclopyr, 255 ppb of trichloropyridinol, and 44 ppb of methoxytrichloropyridine. Three months later, triclopyr had declined about 50%, and the trichloropyridinol had declined about 33%, while methoxy-trichloropyridine increased slightly to 61 ppb. In the next three month interval, between 9 and 12 months after application, triclopyr again declined about 50%, and trichloropyridinol declined 30%, and methoxytrichloropyridine remained about the same. Essentially no residues of any of these compounds were found

below the 0-5 cm zone, except for the 5-15 cm zone contained 67 ppb at the six month sample. The estimated halflifes of triclopyr and trichloropyridinol in the interval between six and 12 months are 70 days and 170 days respectively, in the 0-5 cm soil zone, and the same for triclopyr in the 5-15 cm zone, but greater than 12 months for trichloropyridinol in 5-15 cm zone.

Stream water flowing on the day of application contained up to 80 ppb of triclopyr in the first few hours after application, but the level decreased rapidly to less than 10 ppb at 24 hours. Only one rainfall event occurred within 24 days of application, on day 5, but no residues of triclopyr in the water until day 11, at about 8 ppb and declined thereafter. The stream dried up after day 24 and was dry until fall. There were levels of triclopyr in the dammed water during September and October, even though there was no stream discharge. The maximum level in the water during this time was 12 ppb. The first stream discharge of the fall occurred in November and triclopyr reached levels of 18 ppb in the discharge water. There was strong relation between the amount of triclopyr in water and rainfall events. By use of the flow meters and the concnetration of triclopyr in the water, the authors calculated the percent of applied triclopyr which appeared in the stream discharge during this time and found it to be about 0.003% of applied. Since the stream area was about 0.4% of the total area of the watershed, the authors concluded that the residues of triclopyr in the stream water represented the mobilization of surface residues in the stream bed as opposed to the movement of residues from non-stream bed areas into the bed.

Conclusions:

Overstory vegetation intercepted a large portion of triclopyr application, and thereby prevented an accurate assessment of the dissipation

of triclopyr during the first six months of the experiment. The amount of triclopyr which reaches the soil during the first six months cannot be estimated. Of the triclopyr which does reach the soil the halflife is about 70 days for parent compound and about 170 days for trichloropyridinol. Very little triclopyr was found in stream water, probably only that which was deposited in the area occupied by the stream when flowing.

This report does not suffice as a study of the degradation of triclopyr in the forest environment. The sample intervals are too long apart, samples of the overstory vegetation are not analyzed for residues of triclopyr, ground cover vegetation is not sampled for triclopyr, leaflitter and detritus samples were not sampled for triclopyr While the stream flow may be representative of the locale, it is not representative of either larger watersheds or of eastern forests.

Part 2:

The authors of this report also discuss another small watershed study conducted on a power line right-of-way near Toledo, Oregon. On July 16, 1974, 10.1 kg/ha of triclopyr was applied to unspecified acreage. Water samples were obtained through April of 1975. The maximum amount of triclopyr detected in runoff water was 6 ppb about five months after application and the amount of triclopyr in the runoff water generally declined to about 1 ppb nine months after application.

Conclusions, part 2: The experiment is of limited value. Triclopyr residues are still available to runoff water approximately nine months after application of 9 pounds active per acre, even though the rainfall during the study amounted to over 150 cm of rain.

Reference 16
Residues of Triclopyr; 3,5,6-Trichloro-2-pyridinol and 2-Methoxy-3,5,6-trichloropyridine in Soil and Water From a Watershed Treated with Garlon 3A Herbicide by Aerial Application.
R. L. McKellar, E. J. Norton.
Report No. GH-C-989. April 13, 1977.

Triclopyr as its triethylamine salt in the Garon 3A formulation was applied to a test plot 80 feet by 1200 feet. The applicant states that the treated area is 14.5 acres, whereas the treated area is 2.2 acres contained in a watershed of 14.5 acres. The application was made on June 4, 1974 at the rate of 10 pounds active ingredient per acre by helicopter application. The watershed contained two streams which intersected the treated plot at roughly right angles, on either side of a ridge. The treated plot had vegetation coverage that ranged from open to heavily forested, and samples were obtained from representative areas. Both streams were sampled individually and at a point downstream from their confluence. Soil samples from areas downslope but outside the treated area were also obtained. The residues of triclopyr, and its degradates trichloropyridinol, and methoxytrichloropyridine, were accounted.

Results:

The overstory vegetation intercepted significant amounts of triclopyr, as demonstrated by the differences of residues. In the heavily forested areas, triclopyr was not detectable in the soil on the day of application, while in lightly wooded area, 4.4 ppm of triclopyr was found the day of application, and in the open areas, the residues of triclopyr amounted to 18 ppm in soil. Residues of trichloropyridinol and methoxytrichloropyridine were not detectable in any soil samples in the treated areas on the day of application.

Twenty-eight days after the application, residues of trichloropyridinol

were 0.3 ppm or less in the treated areas and not detectable in any sample interval thereafter. Residues of the other degradate methoxytrichloropyridine, were at trace levels at all sample intervals from day zero to the end of the study.

Residues of parent triclopyr were at trace levels or less at 166 days, 458 days, and 522 days after application of triclopyr.

Outside the treated area, no detectable residues of triclopyr or its degradates were found in any sample site at any sample interval up to the conclusion of the study.

In the water samples, there were no detectable amounts of the degradates trichloropyridinol and methoxytrichloropyridine at any sampling site at any sampling interval. Triclopyr was found in the water samples with a maximum of 0.08 ppm but with the average around 0.01 ppm. Triclopyr residues continued in the water samples through at least day 59 when the flow of the combined streams was low. At higher flow rates, the amount of triclopyr became undetectable in the water, probably due to dilution by rainfall. Applicant does not state whether sediment was removed from the water samples or not.

Conclusions:

Residues of parent triclopyr occur in runoff water up to 2 months after application, but are not detectable during periods of heavy rainfall/runoff. No movement of triclopyr residues outside of the treated areas, except in runoff water. Residues of trichloropyridinol and methoxytrichloropyridine are at trace or below limits of detection.

Reference 17

"The Hydrolysis of Triclopyr in Buffered Distilled Water" by
J.W. Hamaker June 5, 1975 Report DS-1410

A 3.0 ppm solution of ^{14}C-triclopyr subjected to hydrolysis at pH 5.1, 7.2 and 8.3 at 15°C, 25°C, and 35°C. Triclopyr labeled with ^{14}C in 2 and 6 position of ring. Hydrolysis conducted in buffered distilled water. Aliquots were subjected to TLC, followed by counting, to determine hydrolysis products.

Results

No significant hydrolysis of triclopyr at any pH or any temperature over 9 month interval. Several minor photodegradates, less than 1 each were identified as 3,5,6-trichloro-2-pyridinol and 2-methoxy 3,5,6-trichloropyridine. Material balance 90% or better over sampling interval. No information as to possible hydrolysis in natural waters.

Conclusions

Triclopyr is not subject to hydrolysis in buffered distilled water over long intervals.

Reference 18
Bioconcentration of Triclopyr by Catfish in a Static System Containing Soil and Water.
R. W. Meikle, C. R. Youngson, A. J. Regoli.
Report No. GS-1412, October 1, 1975.

Commerce silt loam soil (sand 26, silt 57, clay 17, organic carbon 0.76%, and pH 7.1) was treated at rate of 1.25 ppm (dry wieght basis) which is 1.08 ppm at 100% of 1/3 bar moisture content. Triclopyr was radiolabeled in the 2,6-position with 14C. [Impurity of less than 1% was [redacted] Treated soil was incubated in dark room at 23°C (100% relative humidity) for 30 days, after which the soil-containing aquarium was filled with 156 liters of tap water. An aliquot of soil was placed in graduate and covered with water. This soil aliquot served as submerged soil sample for assay as to soil content at the entry of fish to the aquarium after 35 days of submergence, to avoid disturbing the soil in the aquarium. After 35 days of submergence, 35 black bullhead catfish were placed in aquarium. And after 28 days of exposure, catfish were removed and placed in flowing water for depuration study of 14 days.

Day	Fish	Water	Soil
0-30	---	---	Aerobic
30-65	---	Exposure	Exposure
65-93	Exposure	Exposure	Exposure
93-104	Depuration	---	---

During entire experiment, soil and aquarium water protected from light so that photodegradation would not occur. In addition, the treated soil in the aquarium was covered with aluminum screen separator to prevent stirring up the soil by the catfish. The average weight of the catfish was 3.26 grams and the aquarium load was 0.73 grams of fish per liter. Standard radiometric assay procedures were used. Catfish were divided into edible portions, heads and viscera and skins.

Results:

By the time the catfish were added to the aquarium, at day 65, only 9% of the originally applied 14C was still present in the soil as parent compound, and total 14C was only 28% of applied. Fifteen % of applied 14C was present at this sample interval in the form of 3,5,6-trichloropyridinol. It should be noted that this analysis is on soil in the separate graduate and not on the actual soil in the aquarium.

Parent compound triclopyr does not accumulate in edible portions or in fish heads-viscera-skins of black bullhead catfish. The degradate 2-methoxy-3,5,6-trichloro-2-pyridinol does not accumulate in edible or non-edible portions of catfish. The degradate 3,5,6-trichloro-2-pyridinol does not accumulate in edible portions of catfish, but does accumulate in fish heads-viscera-skins; such accumulation, however, is not signiifcant, since the concentration factor is about 27.

During depuration period oa 12 days, the small amount of 14C in edible portions gradually decreases. In fish heads-viscera-skins, the depuration of 14C-compounds was not investigated.

Conclusions:

Triclopyr and its two known degradates, 2-methoxy-3,5,6-trichloro-2-pyridinol and 3,5,6-trichloro-2-pyridinol do not accumulate to a significant degree in black bullhead catfish.

Reference 19
Determination of the Bioconcnetration Potential of 3,5,6-trichloro-2-pyridinol.
R. T. Hedlund
Report No. GS-1282, November 24, 1972.

Mosquito fish (Gambusia sp) were exposed to 14C-trichloropyridinol in a flow-through system for six days, and then transferred to depuration tanks. The exposure level for the trichloropyridinol was about 1.1 ppb, and was added to the fish tank as an acetone solution by proportional diluter. Whole body fish tissue were extracted by methanolic Soxhlet and radioassayed after tlc.

Results:

Trichloropyridinol is a major photoproduct of triclopyr and may be encountered in the aquatic environment. Trichloropyridinol does not accumulate to any great degree in mosquito fish exposed for six days. An unidentified 14C-material was found in fish at the 12 hour sample and thereafter found in the water sample at the 24 hour sample. The unidentified material from both fish and water had the same zero-R_f value and was presumed to be the same compound. In the water this unknown compound constituted about 3% of the radioactivity, and in the fish it constituted about 30-40 % of the activity.

Conclusions: The photoproduct of triclopyr, trichloropyridinol, does not accumulate to a significant degree in mosquito fish in six days exposure, and depuration occurs rapidly.

Reference 20

Photolysis of Triclopyr (((3,5,6-trichloro-2-pyridinyl)oxy)acetic acid)
J. W. Hamaker
Report No GS-1467, Feb. 11, 1977. Acc. # 229782.

This report is the final report of the experimentation previously reported and submitted under the EUP.. The final report extends the study to photodegradation of triclopyr and its photoproducts and provides material balance not previously reported.

Triclopyr-14C-2,6 labeled was subjected to photolysis in Rayonet photolyzer which closely approximates sunlight. Photolysis was at pH 5.5, 7.1, 8.1 and in canal water. Buffer solutions of triclopyr in vycor glass were also exposed to natural sunlight.

Results:

The halflife of parent triclopyr was found to be less than 10 hours in the photolyzer in the buffer solutions and in the canal water. Photoproducts were found to be trichloropyridinol (up to 10% in the acidic soltuion but less than 3% at 7.1, 8.1, and in canal water), possibly 2-methoxy-3,5,6-trichloropyridinol as small amounts, and 14-CO_2. Up to 25% of the initial 14C was lost from the system as 14-CO_2 during the sampling procedure, and further experimentation with traps showed that the 14C was 14-CO2 rather than volatile materials. Polar material rapidly accrues at the origin of TLC plates, and applicant postulates that polar material at origin is polyhydroxypyridines or further oxidation products such as quinones. This postulation is supported by two other references submitted which describe in detail the photolysis of the trichloropyridinol moiety to polyhydroxypyridines etc. The other two references studied the photolysis of trichloropyridinol as the staring material or as a photoproduct of the insecticide chlorpyrifos.

In natural sunlight studies the halflife of parent triclopyr was found to

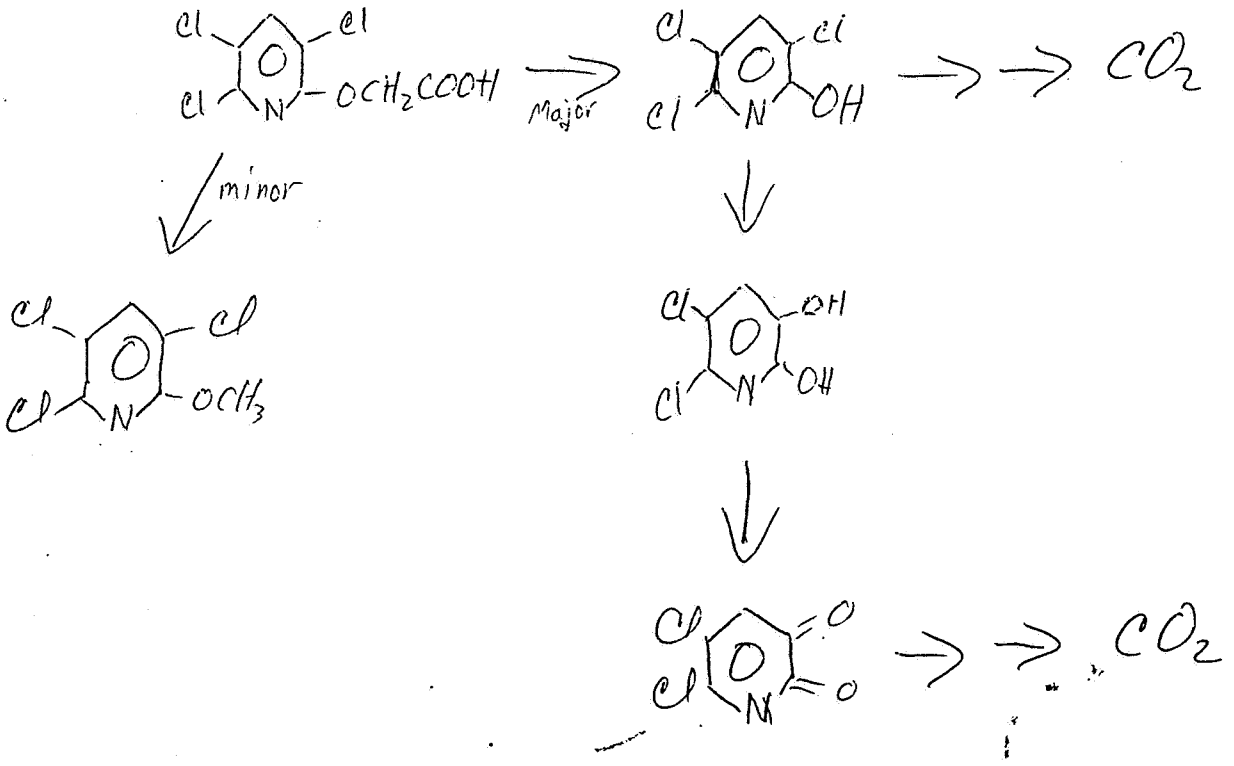
Reference 20

be about two hours of midday sun at Walnut Creek, California. The photoproducts in the natural sun study were the same as in the lab study.

Conclusions:

Parent triclopyr is rapidly photodegraded both in the laboratory and in natural sunlight. The pyridine ring is broken to some degree, within the formation of carbon dioxide. The first photoproduct is trichloropyridinol which is in turn photodegraded at a faster rate than the parent compound. Photolysis of trichloropyridinol yields polar materials shown in other studies to be pyridine polyols from the photolytic hydrolysis of the ring chlorine atoms.

The primary and secondary photoproducts are expected to be further degraded in the environment.



Reference 21

UV Light Decomposition Studies with DURSBAN and 3,5,6-trichloro-2-pyridinol.
G. N. Smith
J. Econ. Ent. 61, p. 793-799. 1968.

This reference describes the photodegradation of the insecticide Dursban and the further photodegradation of the Dursban photoproduct 3,5,6-trichloro-2-pyridinol. The Dursban photoproduct and the major photoproduct from the herbicide Garlon 3A are the same compound. This reference discusses thoroughly the photolysis of trichloropyridinol and is relevant to the phololysis of triclopyr.

Reference 22

The Photodegradation of 3,5,6-trichloro-2-pyridinol (DURSBAN Pyridinol) and the Photodimerization and Photoisomerization of 2-pyridone and Its Monochloro Derivatives.
W. L. Dilling, N. B. Tefertiller, A. B. Mitchell.
Report No. NOW-224-7R.

This reference describes the photodegradation and photoisomerization of 3,5,6-trichloro-2-pyridinol, using model compounds such as 2-pyridone and its monochloro derivatives. This reference is relevant to the photolysis of triclopyr, since 3,5,6-trichloro-2-pyridinol is a photoproduct from the photolysis of triclopyr.

Reference 23
The Effect of Triclopyr on Soil Microorganisms
J. D. Grittith
Report No. GS-1456. September 28, 1976

In vitro agar dish method was used to test the effect of 500 ppm of triclopyr on six soil microorganisms. Growth inhibition of the organisms was compared against untreated controls at 72 hours of incubation.

Results:

There was no apparent effect on any of the following microorganisms: Aerobacter aerogenes, Pseudomonas aeruginosa, Salmonella typhosa, Staphylococcus aureus, Aspergillus terreus, or Pullularia pullulans.

Conclusions:

No apparent effect on six soil microorganisms from triclopyr at 500 ppm. The 500 ppm level greatly exceeds the expected use rate of 9 pounds per acre. This study is not equivalent to the forest use microbial study and can not support a forest use pattern.

Reference 24
Pesticide and Container Disposal Information
Anon. April 1977
Pesticide and Container Disposal Information for Garlon 3A.
The Dow Chemical Company.

This reference contains the "Summary of Interim Guidelines For Disposal of Surplus or Waste Pesticides and Pesticide Containers" as prepared by the Working Group on Pesticides, Washington D. C. June 1972. There is no information specifically on the disposal of triclopyr or its containers. The label does contain disposal information, which is discussed in the Directions for Use section of this evaluation.

4. Conclusions:

Physical-Chemical degradation:

Hydrolysis: Triclopyr is stable to hydrolysis in buffered solutions for periods up to nine months. Chemical hydrolysis is not expected to be a pathway of environmental dissipation.

Photodegradation: Parent triclopyr in aqueous solution is rapidly photodegraded (halflife is less than 24 hours) both in the laboratory and in natural sunlight. The pyridine ring is broken to some degree, with the formation of carbon dioxide. The first photoproduct is trichloropyridinol, which in turn is photodegraded at a faster rate than the parent compound. Photolysis of trichloropyridinol yields polar materials shown in other studies to be pyridine polyols from the photolytic hydrolysis of the ring chlorine atoms. The primary and secondary photoproducts are expected to be further degraded in the aquatic environment. Photodegradation appears to be a major pathway of environmental dissipation, once the compound has reached the aquatic environment.

Metabolism: When the aerobic soil degradation of radiolabeled triclopyr was studied, the parent compound degraded to trichloro-2-pyridinol first, then to trichloromethoxypyridine, and eventually to carbon dioxide with 7-30% evolution at 375 days, dependent upon temperature and moisture content. There was very little unidentified radioactivity in the soil. At expected environmental temperatures, the calculated halflife in the laboratory is between 79 and 361 days, for the transition from parent to first degradate. The halflife from parent through degradates to carbon dioxide is apparently much greater but can not be calculated. Another study confirms first halflife of 79-156 days at 15°C, and shows halflife of less than 50 days at the environmentally improbable temperatures of 25°C and 35°C.
The metabolism of triclopyr results in the formation of 3,5,6-trichloro-2-pyridinol accounting for up to 60% of initial 14C at some intervals, then decline at the longer intervals. At higher soil moisture content, significant amounts of trichloromethoxypyridine were found at longer intervals (17-25% of initial 14C) but much less at lower moisture content. This indicates that trichloromethoxypyridine is formed under more optimum microbial conditions. The trichloromethoxypyridine is considered a secondary degradate produced from the first degradate.
Another indication that microbial metabolism is responsible for degradation is the almost complete lack of degradation of triclopyr in sterilized soil. Under waterlogged conditions, the degradation of triclopyr is considerably slower than in the same aerobic soil. The products of waterlogged triclopyr degradation are the same as aerobic degradation. Significant amounts of triclopyr and its two degradates are found in the water phase of the waterlogged soil study. Organic amendments to soil increased the rate of degradation slightly, but inorganic fertilizer does not.

Another study used plant bioassay technique to show persistence of triclopyr. Use rates of 3 or 9 pounds active per acre showed 50% inhibition for at least 4 months.

In small scale monitoring programs, overstory vegetation intercepted a large portion of the amount applied. The triclopyr which did reach the ground degraded with a halflife of about 70 days, and the degradate trichloropyridinol showed halflife of about 170 days. Runoff water in intermittent stream showed very low amounts of triclopyr. Another test plot showed maximum residues in runoff water at 6 ppb five months after application adn 1 ppb at 9 months, after 150 cm of natural rainfall. A third test plot clearly showed the effects of overstory interception. Triclopyr occurred in runoff water 2 months after application, but not after that probably due to wet-season rainfall dilution of the triclopyr in water. Soil residues of triclopyr declined to trace levels by 166 days. Degradates of triclopyr observed only within 1 month after application. No movement of triclopyr or its degradates was observed.

Accumulation:

Rotational Crops: Rotational crop data is not germane to the proposed use pattern and and not required at this time.

Fish: Black bullhead catfish do not accumulate significant residues of triclopyr or its degradates trichloropyridinol adn trichloromethoxypyridine. Mosquito fish do not accumlate significant residues of trichloropyridinol.

When the triclopyr degradate trichloropyridinol is itself studied for degradation, carbon dioxide is the major degradate and trichlormethoxy-pyridine is minor degradate. The halflife of trichloropyridinol is quite variable from 8-279 days in 15 soils. Twelve of the 15 soils showed half-life of less than 90 days. Two unidentified degradates were found at 1.8%-6.5% of the initial 14C.
The other degradate of triclopyr, trichloromethoxypyridine, when studied by itself, showed extensive degradation to carbondioxide with estimated halflife of 50 days in one soil but more than 300 days in another soil. Trichloropyridinol is also found as a degradate of trichloromethoxypyridine, so apparently the reaction is reversible.
Triclopyr at 500 ppm showed no apparent growth inhibition of six soil microorganisms: Aerobacter aerogenes, Pseudomonas aeruginosa, Salmonella typhosa, Staphlococcus aureus, Aspergillus terreus, Pullularia pullulans. The 500 ppm level greatly exceeds use rate of 9 pounds per acre.
Tank mix degradation studies show no apparent effects on rates of degradation of triclopyr, 2,4-D, or picloram when applied alone or in tank mix combinations.

Mobility:

Leaching: Triclopyr is a leachable compound. Its degradate trichloro-pyridinol is less leachable.

Adsorption/Desorption: Triclopyr has K_d adsorption coefficients ranging from 0.016 to 14.5 in twelve soils, with Koc from 12 to 78; triclopyr is classified as a mobile pesticide.
Trichloropyridinol (degradate of triclopyr) has K_d adsorption coefficients from 0.634 to 5.64, with Koc from 114 to 156, in three soils; this compound is classified as low-to-intermediate mobility.
Desorption of triclopyr is almost complete within 48 hours.

Dissipation:

In dissipation study of six soils under test plot field conditions, parent triclopyr showed apparent halflife average of 46 days with range of 18-84 days. Trichlorpyridinol appeared in 0-6 inch soil layer between 28-56 days and declined thereafter. Other degradate trichloromethoxypyridine at trace levels at all intervals. Soil layers below 6 to 18 inches showed only low levels of triclopyr/degradates. At 400 days after application less than 10% of initial application was present as triclopyr or its two degradates.
In grass/soil test plot using 14C-triclopyr, soil residues of 14C at 428 days were low, less than 0.4 ppm equivalent, and most was in soil organic matter, with less than 0.01 ppm identifiable as triclopyr or trichloro-pyridinol. In grass at 128 days, total triclopyr and conjugated triclopyr were less than 0.1 ppm.

5. Recommendations

1. The proposed use pattern on certain non-crop areas is supported by adequate environmental chemistry data to understand the fate of the chemical in the environment. The use supported by the environmental chemistry data are: non-crop areas including industrial manufacturing and storage sites, rights-of-way such as electrical power lines, communication lines, pipelines, roadsides and railroads.

2. It cannot be determined if the proposed use pattern on forests is supported by adequate environmental chemistry data to understand the fate of this compound in the forest environment. The label of the proposed product is vague in the definition of forests, with the only clue as to its meaning appearing in the directions for use in "Forest Site Preparation". It is understood that Herbicide Efficacy Section has requested clarification of this same point. If the use pattern 'forests' is actually intended to be reforestation sites, the label should so state this clearly. If the use pattern 'forests' is not reforestations sites, the intent of the use pattern must still be clarified. Attached is an example of an appropriate protocol for determining environmental fate of a compound in the forest environment. We defer to Environmental Safety Section regarding their need for such environmental chemistry data in their assessment of the hazard of the compound in the environment.

Ronald E. Frey for 7/6/78

R. W. Cook 6-28-78

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Environmental Chemistry Section
Efficacy and Ecological Effects Branch

Forest Uses:

Forest uses patterns require a field ecosystem residue study using the formulated pesticide product to assess environmental fate and hazard. Environmental components of the field ecosystem residue study to be monitored include: foliage, leaf litter, litter-covered soil, exposed soil, standing (pond) water, moving (stream) water, sediments, fish, and other aquatic organisms. The components of the field ecosystem residue study are monitored for residues of parent compound and known degradates of the parent compound, using appropriate analytical techniques. One field location representative of the treated area is sufficient for the field ecosystem residue study. Additional sites may be needed if the proposed use includes widely differing forest types. Data between various forest types should be extrapolated. Sampling times include pre-application, day of application, and post-application, to construct decline curves for residues in foliage, leaf litter, soil, and standing water. When analyses of successive leaf litter, soil, and standing water samples show residues at the level of method sensitivity, and foliage samples indicate that greater than ninety percent of initial residues have dissipated, sampling may be terminated. Sampling need not be as frequent for sediments, running water, and aquatic organisms. To determine pesticide movement in forest floor environments, exposed soil shall be sampled to 15 cm, and litter-covered soil to 8 cm, over a two-week period following natural precipitation.

An example of appropriate experimental design can be found in:

Giles, P.H. Jr. 1970. The ecology of a small forested watershed treated with the insecticide malathion-S^{35}. Wildlife Monograph No. 24. The Wildlife Society, Washington, D.C. The information contained in the reference is more extensive than generally required, however, the basic design is adequate. The applicant is not required to use radiolabeled compounds as were used in the referenced study.